

PLASMA CHEMISTRY AND ORGANIC SYNTHESIS

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| 16. Abstract<br>The characteristic features of chemical reactions using low-temperature plasmas are described and differentiated from those seen in other reaction systems. A number of examples of applications of plasma chemistry to synthetic reactions which have been reported recently are mentioned. The production of amino acids by discharge reactions in hydrocarbon-ammonia-water systems is discussed, and its implications for the origins of life are mentioned. |  |  |           |
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# PLASMA CHEMISTRY AND ORGANIC SYNTHESIS

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## 1. Introduction

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"Plasma" here is defined as "an ensemble of more or less neutral particles including charged particles" [1]. Ordinarily, however, the term is used to refer to what we encounter in the form of discharge gases.

Concerning the relations between plasma and chemistry, research has been under way for some time on the elementary process of the reactions in terms of discharge chemistry. However, the connections with organic chemistry, especially with the field of synthesis, in the past have not been necessarily very deep. Besides the manufacturing of acetylene by means of arc discharge, probably the only connection was with silent discharge during the oxidation of ozone. However, in recent years rapid advances have been made in application to the field of materials science of plasmas, especially those which are known as "low-temperature plasmas." New technologies have been developed, such as the dry etching method in the process of integrated circuit manufacturing, plasma polymerization for manufacturing high-molecular thin films, and modification and reforming of the surfaces of various solid materials. This has finally heightened the interest of organic chemists in the chemical reactions which occur in plasma, and attempts at seeking out the possibilities for new synthetic reactions have come to be quite active.

In this paper, the author wishes to describe simply the characteristic features of the organic plasma reactions which are regarded in this fashion as "young chemistry" with great future potentialities. Of the research carried out recently, he wishes to introduce chiefly studies dealing with synthetic reactions. In addition, he will also

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\* Numbers in the margin indicate pagination in the foreign text.

deal with some interesting studies which have been made on the connections between chemical evolution and plasma reactions.

Incidentally, an excellent general survey has been published in recent years concerning the applied technologies [2]. The reader is also referred to the other general articles in this special issue for information about the utilization of plasma in inorganic chemistry and polymer chemistry.

## 2. Plasma and Organic Chemistry

The plasmas which are ordinarily utilized in organic chemical reactions are those belonging to the category of the so-called low-temperature plasmas, such as glow discharge or corona discharge. In these low-pressure discharge gases, the electrons have a remarkably great kinetic (thermal) energy, while the neutral molecules and ions have only a much lower energy.

This state in which high-temperature ( $10^4 - 10^5$  K) electrons are flying around in a gas which has normal or near-normal temperature is called a "low-temperature plasma" or an "unbalanced plasma."

On the other hand, arc discharges and plasma jets are called "thermal plasma" or "balanced plasma." Since the gases have a high temperature close to the temperature of the electrons, they have a considerably limited application to organic chemistry, which deals with substances which are thermally not very stable.

High-frequency discharges are also a type of low-temperature plasma. In this case, the electric field is reversed before the electrons reach the electrode, so that the electrons will be captured in the space. As a result, the discharge will continue even in the absence of an electrode. Discharges of this type can be carried out without using electrodes, and the reaction factors can be simplified. In addition, high-frequency power sources have become relatively easily available. For these and other reasons, this type of discharge has been adopted in almost all organic plasma reactions recently.

The characteristic features of chemical reactions in these low-temperature plasmas include, first of all, the fact that they are vapor phase reactions at low temperatures (about  $1 - 10^{-2}$  mm Hg). Some attempts have been made to accelerate the reactions by introducing into the condensed phase the active species produced in the plasma, but even in these cases the first stage of the reaction takes place in the vapor phase. For this reason, it is desirable for the reaction substrate to be a substance which has a vapor pressure of a certain degree in the vicinity of normal temperature, but even if the substance has a quite low vapor pressure the goal can still be attained by heating the reaction system as a whole to a suitable temperature and keeping it at this temperature.

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A second characteristic feature is the fact that, in a plasma reaction, the reaction is started primarily as a result of collisions between vapor-phase molecules and high-energy electrons. This is a point where these reactions differ greatly from ordinary thermochemical reactions, in which collisions between molecules are an important process of activation. Part of the kinetic energy of the electrons is transformed into internal energy of the molecules by the inelastic collisions with the molecules. The processes of ionization of the molecules or of excitation (electrons, vibrations, at the rotation level) proceed in accordance with the magnitude of the amount of energy transformed. If the atoms or molecules have a great electron affinity, anions are sometimes produced by electron adhesion. The electrons are also extinguished by recombination with the ions on the vessel walls or in the vapor phase, and the energy discharged at this time becomes an excitement or radiation energy. The ions and excited species produced by these processes give rise to even more highly varied active species as a result of secondary dissociation or ion-molecule reactions. In addition, auxiliary photochemical reactions caused by the radiation energy also proceed.

One of the most important factors in these seemingly complex plasma reactions is the electron energy operating at the beginning stage. It is anticipated that this energy is distributed over a quite broad range, and it is ordinarily approximated to a Maxwell or Druyvesteyn distribution [3]. In low-temperature plasmas under ordinary conditions, the

average electron energy is estimated to range from several eV to about 10 eV.

Table shows bond energy in typical organic compounds. Table 2 shows the ionization potential and the singlet and triplet minimum excitation energy for a number of compounds. It is clear from these data that low-temperature plasmas are in an energy level state suitable for anticipating that these processes would move ahead.

TABLE 1.  
BOND ENERGY OF ORGANIC COMPOUNDS

| 結合  | エネルギー<br>(eV) | 結合   | エネルギー<br>(eV) |
|---|---------------|--|---------------|
| H-CH <sub>3</sub>                               | 4.5           | CH <sub>2</sub> =CH <sub>2</sub>               | 10.0          |
| H-C <sub>2</sub> H <sub>5</sub>                 | 4.2           | CH <sub>2</sub> =CH <sub>2</sub>               | 7.5           |
| H-CHCH <sub>3</sub>                             | 4.7           | CH <sub>3</sub> -CH <sub>3</sub>               | 3.8           |
| H-CCH   | 5.4           | CH <sub>3</sub> -C <sub>2</sub> H <sub>5</sub> | 4.3           |
| H-C <sub>2</sub> H <sub>5</sub>                 | 4.8           | CH <sub>3</sub> -CN                            | 5.4           |
| H-CP <sub>2</sub> C <sub>2</sub> H <sub>5</sub> | 3.7           | CH <sub>3</sub> -OH                            | 3.9           |
| H-CH <sub>2</sub> OH                            | 4.1           | CH <sub>3</sub> -Cl                            | 3.6           |
| H-CH <sub>2</sub> COCH <sub>3</sub>             | 4.3           | CH <sub>3</sub> -Br                            | 3.0           |
| H-OCH <sub>3</sub>                              | 4.5           | CH <sub>3</sub> -I                             | 2.4           |
| H-OC <sub>2</sub> H <sub>5</sub>                | 3.8           | C <sub>2</sub> H <sub>5</sub> -Cl              | 4.1           |

Key:

1. Bond
2. Energy (eV)

TABLE 2.  
IONIZATION POTENTIAL AND MINIMUM EXCITATION  
ENERGY OF SINGLETS ( $E_S$ ) AND TRIPLETS ( $E_T$ )

| 1 化 合 物    | $I_P$ (eV) | $E_S$ (eV) | $E_T$ (eV) |
|------------|------------|------------|------------|
| 2 アントラセン   | 7.23       | 3.3        | 1.8        |
| 3 ベンゼン     | 9.25       | 4.8        | 3.7        |
| 4 トルエン     | 8.82       | 4.6        | 3.6        |
| 5 アセトフェノン  | 9.27       | 3.4        | 3.2        |
| 6 アニリン     | 7.70       | 4.2        | 3.3        |
| 7 フェノール    | 8.50       | 4.5        | 3.5        |
| 8 クロロベンゼン  | 9.07       | 4.6        | 3.5        |
| 9 ベンズアルデヒド | 9.53       | 3.3        | 3.1        |
| 10 スチレン    | 8.47       | 4.3        | 2.7        |
| 11 安息香酸    | 9.73       | 4.4        | 3.4        |

Key:

1. Compound
2. Anthracene
3. Benzene
4. Toluene
5. Acetophenone
6. Aniline
7. Phenol
8. Chlorobenzene
9. Benzaldehyde
10. Styrene
11. Benzoic acid

Considered from the standpoint of energy supply, a plasma reaction can be regarded as a conversion from electrical energy to chemical energy. It differs greatly from an electrochemical reaction of the past in the following points. First, the reaction system is in the vapor phase, not in the condensed phase. In addition, the electrons taking part in the reaction are supplied from the reaction system itself, and there is no reliance on an exchange with an external power source. This is especially true in high-frequency discharges. Finally, the electrons are extinguished within the system.

Furthermore, in a photochemical reaction or a radiation chemical reaction, the reaction proceeds as a result of direct introduction of an energy carrier into the reaction system from the outside. On the other hand, a plasma reaction assumes a highly peculiar form in which the energy is supplied through the form of the kinetic energy of the electrons.

One may also say that the greatest attractiveness of plasma organic reactions, as well as their difficulty, consists precisely in these distinctive features which are not seen in other methods of reaction.

### 3. Applications to Synthetic Reactions

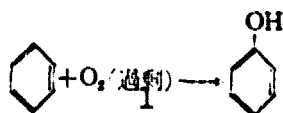
In recent years active research has been under way with attention being paid to the distinctive features of organic plasma reactions described in the preceding section, and a considerable number of examples of reactions have also been accumulated. Because of limitations of space here, let us select and introduce only the very latest studies. / Other general works give details of the research performed before this [4]. Most of the latest research has been performed by the flow method, and the main discharge system is the high-frequency discharge system using radio waves or microwaves.

The high-frequency output is ordinarily several tens to 100 W, and the product yields are about several tens of grams per hour under the optimum conditions. Even though a considerable distance must still be traversed before practical application can be realized, one may say that



the reactions have reached a rather advanced stage for reactions on the laboratory scale.

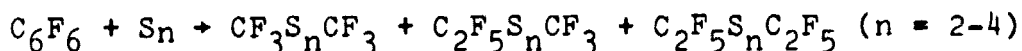
First, among the most interesting reactions are the addition reactions and substitution reactions which utilize active species produced by plasma. Reactions using oxygen or nitrogen in the atomic state have been reported for a rather long time. Quite recently, there have been examples of direct synthesis of phenol by the oxidation of benzene [5].



Key:  
1. (excess)

Cases have been reported in which plasma has been used for mono-fluorination of an aromatic ring [6]. When trifluoromethylbenzene is catalyzed downstream from a fluorine plasma, fluorine is introduced into the benzene ring. When the amount of fluorine was less than 10 times the amount of the reaction substrate, mixtures of isomers were produced, but when the amount of fluorine was more than 10 times the para form was produced with a 100% selectivity and a 30% yield. It is explained that this is attributable to the great electronegativity of the trifluoromethyl group and to the steric effect.

Reactions for synthesis of polysulfides have also been reported [7]. When a mixed steam of hexafluoroethane and sulfur was treated by radio wave discharge, polysulfides ( $S_2 - S_4$ ) were obtained.



Another interesting reaction is the cyano conversion reaction of aromatic compounds in which acetonitrile was used as the cyano source [8]. Plasma reactions of acetonitrile have been studied in the presence of various types of aromatic compounds. In cases where excessive acetonitrile is present, the reaction of the aromatics themselves is inhibited, and aromatic nitriles are produced with a quite high yield (Table 3).

The effects of the reaction factors, the percentages of isomers present 23 and the kinetic results are being discussed in connection with the reaction mechanism.

TABLE 3.  
YIELDS OF AROMATIC NITRILES FROM ACETONITRILE

| 1 基 質   | 2 転化率 (%) | 3 トリル収率 (%) |
|---------|-----------|-------------|
| 4 ベンゼン  | 76        | 61          |
|         | 32        | 85          |
| 5 トルエン  | 81        | 21          |
|         | 50        | 38          |
| 6 ナフタレン | 49        | 83          |
| 7 ピリジン  | 16        | 60          |
| 8 チオフェン | 30        | 40          |

Key:

1. Substrate
2. Conversion rate (%)
3. Nitrile yield (%)
4. Benzene
5. Toluene
6. Naphthalene
7. Pyridine
8. Thiophene

One of the plasma reactions which seems to be promising with respect to synthesis is the elimination reaction. Elimination of small molecules such as carbon monoxide or carbon dioxide is an extremely common reaction in plasma reactions [9]. Saturated hydrocarbons easily produce unsaturated compounds, but the selectivity is usually not very high. An even more interesting reaction is the synthesis of three-member or four-member chain compounds from cyclic ketones or lactones [10] (Fig. 1).

The same reactions are also known with respect to quinones [11] (Fig. 2).

In these reactions, it is supposed that biradicals are produced along with elimination as intermediates.

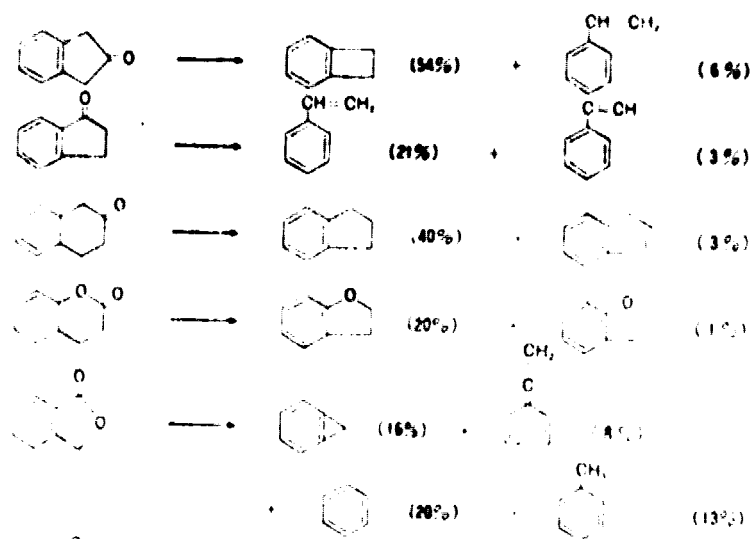


Fig. 1.

Fig. 1.

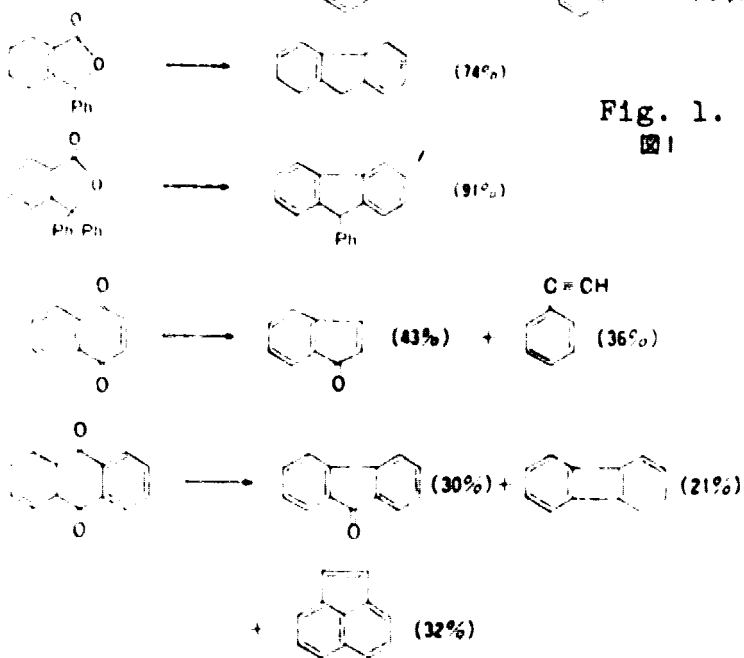
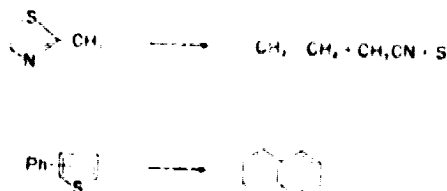


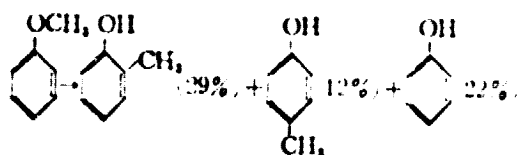
Fig. 2.

There are also many reports concerning desulfurization. Mercaptans and thiophenols will easily liberate sulfur in the form of hydrogen sulfide or of the simple substance without undergoing polymerization or carbonization [12]. Sulfur dioxide is also easily eliminated from sulfones [13]. There have also been some reports of elimination of sulfur from complex rings [14].



Isomerization reactions also are common plasma reactions. Cis-butene-2 will be isomerized into trans-butene-2 and butene-1 almost quantitatively under conditions of a low conversion rate. Under conditions where there is a high conversion rate, there will be larger amounts of decomposition products. The cis isomer and butene-1 have also been obtained in the same way from trans-butene-2 [15].

The conversion reactions of alkyl phenyl ethers have also been investigated in detail. It is supposed that the reactions proceed in accordance with a radical cleavage-recombination mechanism [16].



Examples of stereospecific reactions are the cyclization reactions of cis, cis, trans-octatriene into trans-cyclohexadiene [17].



#### 4. Connection with Chemical Evolution

It has already been pointed out for a long time that electric discharges have a profound connection with the origins of organic compounds on the earth and with the origins of life. It is thought that a discharge phenomenon such as a flash of lightning on the primeval earth could have plasmified the atmospheric components, resulting over a prolonged period of time in synthesis of simple organic substances or amino acids. In actual fact, it has been observed that numerous types of amino acids are produced when discharge reactions are carried out in systems containing various types of hydrocarbons as well as ammonia and water, which also happen to be the components of the primeval atmosphere [18].

Examples of amino acids which are produced are shown in Table 4. There are also reports that purine bases and pyrimidine bases [19], or porphyrin-like substances [20] have been detected in similar reaction systems. It has also been reported that the production of amino acids has been accelerated by the presence of clay [21].

TABLE 4.  
AMINO ACIDS PRODUCED BY DISCHARGE REACTIONS  
IN HYDROCARBON-AMMONIA-WATER SYSTEMS

| 1<br>アミノ酸      | 2<br>炭化水素 | 3<br>メタン | 4<br>エタン | 5<br>エチレン | 6<br>アセチレン |
|----------------|-----------|----------|----------|-----------|------------|
| 7<br>グリシン      | ○         |          |          | ○         | ○          |
| 8<br>アラニン      | ○         |          | ○        | ○         | ○          |
| 9<br>β-アラニン    | ○         |          |          | ○         | ○          |
| 10<br>α-アミノ酪氨酸 | ○         | ○        |          | ○         | ○          |
| 11<br>バリン      | ○         | ○        |          | ○         | ○          |
| 12<br>ノルバリン    | ○         | ○        |          |           | ○          |
| 13<br>ロイシン     |           |          |          | ○         | ○          |
| 14<br>イソロイシン   |           |          |          | ○         | ○          |
| 15<br>アスパラギン酸  | ○         |          |          |           |            |
| 16<br>グルタミン酸   | ○         |          |          |           | ○          |
| 17<br>フェニルアラニン |           | ○        | ○        |           | ○          |

Key: 1. Amino acid  
2. Hydrocarbon  
3. Methane  
4. Ethane  
5. Ethylene  
6. Acetylene  
7. Glycine  
8. Alanine  
9. Beta-alanine  
10. Alpha-amino-butyric acid  
11. Valine  
12. Norvaline  
13. Leucine  
14. Isoleucine  
15. Aspartic acid  
16. Glutamic acid  
17. Phenylalanine

When micro-wave discharges are performed in acetylene-ammonia- /352  
hydrogen systems, a group of highly unsaturated, linear molecules which  
have the structure  $\text{H}(\text{C}\equiv\text{C})_n\text{CN}$  are produced together with hydrogen cyanide  
[22]. It is known from radiometeorological observations that these  
substances are present in interstellar space. If the origin of these  
interstellar substances can also be sought in plasma reactions, it would  
be no exaggeration to say that plasma reactions are precisely the point  
of origin of chemical reactions.

## 5. In Conclusion

As is usually the case in new sciences, in the field of plasma  
chemistry as well, systematic fundamental research concerning organic  
plasma reactions has only recently begun, although the applied techno-  
logies have already made their head start. As was mentioned above, many  
unique reactions are being discovered, but many problems still remain to  
be solved before the stage of practical application can be reached.  
While discharges under normal pressure such as arc discharges have  
already been put into practical application, such as in the manufacturing  
of acetylene from coal, low-temperature plasma operations are conducted  
at a low pressure, and this is quite disadvantageous for the operating  
efficiency of the reactors. In addition, the engineering problems such  
as the problem of increasing the scale of the reactors or optimizing the  
reaction factors still remain as topics for future study. Furthermore,  
since plasma reactions are reactions of the energy consuming type, in  
the future period of expensive electricity it will be necessary to make  
redoubled efforts to develop specific reactions which cannot be achieved  
by other methods and to produce substances which will have a great added  
value.

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